

HYDRODESULFURIZATION CATALYST AND PROCESSES THEREFOR AND THEREWITH

The present invention relates to a catalyst for hydrodesulfurizing hydrocarbon streams and processes therefor and therewith.

Background of the Invention

Naphtha streams are primary products in petroleum refineries. These naphtha streams are typically blended to make up what is referred to in the industry as the "gasoline pool". Naphtha streams contain valuable olefins and aromatics which contribute to the octane number of the gasoline pool. However, one problem associated with such naphtha streams, especially those which are products of a cracking process, such as fluidized catalytic cracking, is that they contain relatively high levels of sulfur. Although cracked naphthas typically constitute less than 40 percent of the total gasoline pool, cracked naphthas frequently contribute over 70 percent of the sulfur to the gasoline pool.

Due to ever stricter government regulations limiting the amount of sulfur in gasoline, there is a continuing need for improved processes and catalysts for hydrodesulfurizing hydrocarbon streams so that the sulfur level of the gasoline pool can be lowered. Although a variety of hydrodesulfurization processes and catalysts are in commercial use today, conventional hydrodesulfurization processes capable of removing a substantial amount of sulfur from hydrocarbon streams typically cause significant octane loss. Thus, there exists a continuing need for improved hydrodesulfurization processes and catalysts which maximize sulfur removal while minimizing octane loss.

Summary of the Invention

An object of this invention is to provide a process and catalyst for hydrodesulfurizing a hydrocarbon stream, whereby the conversion of organic sulfur compounds to inorganic sulfur compounds is maximized while octane loss is minimized.

A further object of this invention is to provide a process and catalyst for hydrodesulfurizing a hydrocarbon stream, whereby the conversion of organic sulfur compounds to inorganic sulfur compounds is maximized while saturation of aromatic compounds is minimized.

A still further object of this invention is to provide a process and catalyst for hydrodesulfurizing a hydrocarbon stream, whereby the conversion of organic sulfur compounds to inorganic sulfur compounds is maximized while saturation of olefins is minimized.

An even further object of the present invention is to provide a method for making an improved hydrodesulfurization catalyst.

Further objects and advantages of the present invention will become apparent from consideration of the detailed description of the invention and appended claims.

In accordance with a first embodiment of the present invention, a catalyst composition is provided which comprises a nitrated and sulfided composition comprising a cobalt compound, a molybdenum compound, and an inorganic oxide compound.

In a second embodiment of the present invention, a process of making a catalyst composition is provided. The process comprises incorporating a cobalt compound and a molybdenum compound into an inorganic oxide compound, nitrating the cobalt/molybdenum-modified catalyst, and sulfiding the nitrated cobalt/molybdenum-modified catalyst.

In a third embodiment of the present invention, a hydrodesulfurization process is provided. The hydrodesulfurization process comprises contacting a hydrocarbon feed containing a concentration of organic sulfur compounds and a concentration of aromatic compounds with a catalyst composition comprising a nitrated and sulfided composition comprising a cobalt compound, a molybdenum compound, and an inorganic oxide compound under conditions sufficient to convert at least a portion of the organic sulfur compounds to inorganic sulfur compounds.

In a fourth embodiment of the present invention, a hydrodesulfurization process is provided. The process comprises separating a full range hydrocarbon feed containing organic sulfur compounds and aromatic compounds into a heavy hydrocarbon fraction and a light hydrocarbon fraction, contacting the heavy hydrocarbon fraction with a catalyst composition comprising a nitrided and sulfided composition comprising a cobalt compound, a molybdenum compound, and an inorganic oxide compound under conditions sufficient to convert at least a portion of the organic sulfur compounds to inorganic sulfur compounds, and combining the hydrodesulfurized heavy hydrocarbon product with the light hydrocarbon fraction to produce a hydrodesulfurized full range hydrocarbon product.

Detailed Description of the Invention

According to a first embodiment of the present invention, a catalyst composition comprising a nitrided and sulfided composition comprising a cobalt compound, a molybdenum compound, and an inorganic oxide compound is provided.

The cobalt compound and molybdenum compound of the inventive catalyst composition may be present either in elemental form or any other suitable form. The amount of cobalt compound present in the inventive catalyst composition is preferably such that the weight of the cobalt component of the cobalt compound as a percentage of the total weight of the catalyst composition is from about 0.1 percent to about 30 percent, more preferably from about 0.5 percent to about 10 percent, and most preferably from 1 percent to 5 percent. The amount of molybdenum compound present in the inventive catalyst composition is preferably such that the weight of the

molybdenum component of the molybdenum compound as a percentage of the total weight of the catalyst composition is from about 1 percent to about 50 percent, more preferably from about 2 percent to about 25 percent, and most preferably from 3 percent to 15 percent. The atomic ratio of cobalt to molybdenum in the inventive catalyst is preferably from about 0.1:1 to about 10:1, more preferably from 0.2:1 to 2:1.

The inventive catalyst composition further comprises an inorganic oxide compound. Examples of inorganic oxide compounds include Groups II, III, IV or V metal oxides. Preferably, the inorganic oxide is inert. More preferably, the inorganic oxide is selected from the group consisting of silica, alumina, silica-alumina, magnesia, titania, zirconia, and mixtures of two or more thereof. Most preferably, the inorganic oxide compound is γ -alumina. The inventive catalyst composition preferably contains from about 10 weight percent to about 95 weight percent inorganic oxide compound, more preferably from 50 weight percent to 90 weight percent inorganic oxide compound, and most preferably from 75 weight percent to 85 weight percent inorganic oxide compound.

The inventive catalyst composition is nitrided, preferably pre-nitrided. As used herein, the term "pre-nitrided" means that nitridation of the catalyst occurred before contacting the catalyst with a sulfur-containing hydrocarbon stream under hydrodesulfurization conditions. The inventive catalyst composition is preferably nitrided in a manner such that the nitrogen component of the metal nitride(s) is present in an amount such that the final catalyst composition contains from about

0.001 weight percent to about 10 weight percent nitrogen, more preferably from 0.1 weight percent to 2 weight percent nitrogen.

The inventive catalyst composition is sulfided, preferably pre-sulfided. As used herein, the term "pre-sulfided" means that sulfidation of the catalyst occurred before contacting the catalyst with a sulfur-containing hydrocarbon stream under hydrodesulfurization conditions. The inventive catalyst composition is preferably sulfided in a manner such that the sulfur component of the metal sulfide(s) is present in an amount such that the final catalyst composition contains from about 0.1 weight percent to about 10 weight percent sulfur, more preferably from 1 weight percent to 5 weight percent sulfur.

According to a second embodiment of the present invention, a process for making a catalyst composition is provided. The process comprises the steps of incorporating a cobalt compound and a molybdenum compound into an inorganic oxide compound, nitriding the cobalt/molybdenum-modified catalyst composition, and sulfiding the nitrified cobalt/molybdenum-modified catalyst composition.

The cobalt compound and molybdenum compound can be incorporated into the inorganic oxide compound in any suitable manner known in the art such as, for example, equilibrium adsorption, incipient wetness impregnation, pore filling, or ion exchange. Preferably, the cobalt compound and molybdenum compound are incorporated in inorganic oxide compound by incipient wetness impregnation. The cobalt compound and molybdenum compound can be incorporated in the inorganic

oxide compound either sequentially or simultaneously, with simultaneous impregnation being the preferred method.

Preferably, the incorporation of the cobalt compound and the molybdenum compound into the inorganic oxide compound is accomplished by contacting the inorganic oxide compound with an aqueous solution containing both the cobalt compound and the molybdenum compound. Examples of cobalt compounds suitable for use in the incorporation step include, but are not limited to, cobalt nitrate, cobalt acetate, cobalt carbonate, cobalt oxide, cobalt sulfate, cobalt thiocyanate, and the like and mixtures of any two or more thereof. Examples of molybdenum compounds suitable for use in the incorporation step include, but are not limited to, ammonium heptamolybdate, ammonium molybdate, sodium molybdate, potassium molybdate, molybdenum oxides such as molybdenum (IV) oxide and molybdenum (VI) oxide, molybdenum sulfide, and the like and mixtures of any two or more thereof. Preferably, the aqueous solution contacted with the inorganic oxide compound comprises cobalt nitrate and ammonium heptamolybdate.

It is preferred for the incorporation of the cobalt compound and molybdenum compound into the inorganic oxide to be accomplished using two impregnations. After each impregnation, the cobalt/molybdenum modified catalyst can be dried at about 80°C to about 250°C, preferably 100°C to 150°C, for about 0.5 hours to about 20 hours, preferably 1 hour to 5 hours. After each impregnation it is preferred for the cobalt/molybdenum-modified catalyst to be calcined at about 300°C

to about 900°C, preferably 400°C to 600°C, for about 0.5 hours to about 10 hours, preferably 2 hours to 4 hours.

Before being used in a hydrocarbon desulfurization process, the cobalt/molybdenum-modified catalyst is preferably pre-nitrided. Preferred pre-nitriding methods include, for example, flowing an easily decomposable nitrogen-containing compound over the catalyst at elevated temperatures. Preferably, pre-nitriding is accomplished by flowing a decomposable nitrogen-containing compound over the catalyst at a temperature of from about 650°C to about 800°C for a time period of from about 0.5 hours to about 5 hours. Most preferably, pre-nitriding is accomplished by flowing ammonia over the catalyst at a temperature of from 675°C to 750°C for a time period of from 1 hour to 3 hours.

Before being used in a hydrocarbon desulfurization process, the pre-nitrided cobalt/molybdenum-modified catalyst is preferably pre-sulfided. Preferred pre-sulfiding methods include, for example, heating the catalyst in a stream of hydrogen sulfide and hydrogen or by flowing an easily decomposable sulfur compound such as carbon disulfide, di-*n*-nonylpolysulfide (TNPS) or dimethyldisulfide with or without a hydrocarbon solvent, over the catalyst at elevated temperatures up to, but not limited to 500°C at atmospheric or higher pressures, in the presence of hydrogen gas for 0.5 to 10 hours. Most preferably, pre-sulfiding is accomplished by contacting the nitrided cobalt/molybdenum-modified catalyst with a carbon disulfide-saturated stream of hydrogen for 1 hour to 5 hours at a temperature of from 350°C to 450°C.

In accordance with a third embodiment of the present invention, a hydrodesulfurization process is provided which comprises contacting a hydrocarbon feed with a catalyst composition comprising a nitrated and sulfided composition comprising a cobalt compound, a molybdenum compound, and an inorganic oxide compound.

The feed to the hydrodesulfurization process of the present invention is preferably an organic sulfur-containing hydrocarbon feed that boils in the gasoline boiling range. Examples of organic sulfur-containing hydrocarbon feeds suitable for use in the process of the present invention include thermally cracked naphthas such as pyrolysis gas, coker naphtha, and visbreaker naphtha, as well as catalytically cracked naphthas such as thermofor catalytic cracking (TCC) or fluid catalytic cracking (FCC) naphtha. Preferably, the organic sulfur-containing hydrocarbon feed is catalytically cracked naphtha, most preferably FCC naphtha boiling in the range of from 80°F to 500°F.

The organic sulfur compounds present in the organic sulfur- containing hydrocarbon feed can be represented by the formula RSR'. RSR' is preferably (1) a thiol or mercaptan, where R is a hydrocarbyl and R' is hydrogen, (2) a sulfide or disulfide, where the sulfur is connected to another sulfur atom in R or R' hydrocarbyl groups, and/or (3) a thiophene, where R and R' are connected to form a heterocyclic ring.

During hydrodesulfurization, the desired reaction is the reaction of organic sulfur compounds with hydrogen to produce inorganic sulfur compounds,

typically hydrogen sulfide. However, one problem associated with conventional hydrodesulfurization processes is that olefinic and aromatic compounds present in the hydrocarbon feed also react with hydrogen, resulting in saturation of the olefins and aromatics. This saturation of olefins and aromatics can dramatically decrease the octane number of the hydrocarbon stream being processed.

In most organic sulfur-containing hydrocarbon streams, such as cracked naphthas, the majority of the olefinic compounds are present in the light hydrocarbon fraction, while the majority of the aromatic and organic sulfur compounds are present in the heavy hydrocarbon fraction. It has been discovered that sulfur can be removed from a hydrocarbon stream with minimal olefin saturation by hydrodesulfurizing only the heavy hydrocarbon fraction. In order to ensure adequate desulfurization of the heavy hydrocarbon fraction without a significant loss in octane, the heavy hydrocarbon fraction is preferably contacted with a hydrodesulfurization catalyst which is effective to maximize the conversion of organic sulfur compounds to inorganic sulfur compounds, while minimizing the conversion of aromatic compounds to non-aromatic compounds.

In accordance with a fourth embodiment of the present invention, a process is provided which comprises separating a full range hydrocarbon stream into a heavy hydrocarbon fraction and a light hydrocarbon fraction, hydrodesulfurizing the heavy hydrocarbon fraction by contacting it with a catalyst composition comprising a nitrided and sulfided composition comprising a cobalt compound, a molybdenum

compound, and an inorganic oxide compound, and recombining the hydrodesulfurized heavy hydrocarbon fraction with the light hydrocarbon fraction.

A "cut point temperature" is employed to separate the full range hydrocarbon fraction into a heavy hydrocarbon fraction (boiling above the cut point temperature) and a light hydrocarbon fraction (boiling below the cut point temperature). The cut point temperature can vary according to the organic sulfur compounds present and the degree of desulfurization required. A cut point temperature in the range of from about 150°F to about 350°F is preferred, with a cut point temperature in the range of 200°F to 300°F being most preferred. Cut point temperatures towards the lower end of the given range will typically be necessary for lower product sulfur specifications while cut point temperatures towards the upper end of the given range may be used to minimize octane loss.

The full range hydrocarbon feed employed in the present invention typically boils in the range of from about 80°F to about 500°F, more typically from 100°F to 450°F. The full range hydrocarbon feed preferably contains aromatic compounds in an amount such that the weight of aromatic compounds as a percentage of the weight of the total full range hydrocarbon feed is from about 10 percent to about 50 percent, more preferably from 20 percent to 40 percent. The full range hydrocarbon feed preferably contains olefinic compounds in an amount such that the weight of olefinic compounds as a percentage of the weight of the total full range hydrocarbon feed is from about 10 percent to about 50 percent, more preferably from 15 percent to 40 percent. The concentration of sulfur in the full range hydrocarbon

feed is preferably from about 5 ppmw to about 5000 ppmw, more preferably from 50 ppmw to 1000 ppmw. Most preferably, the full range hydrocarbon feed is catalytically cracked naphtha.

The heavy hydrocarbon fraction preferably boils in the range of from about 200°F to about 500°F, more preferably from 250°F to 450°F. The heavy hydrocarbon fraction preferably contains a concentration of aromatic compounds such that the weight of aromatic compounds as a percentage of the total weight of the heavy hydrocarbon fraction is greater than about 10 percent, more preferably from about 10 percent to about 95 percent, still more preferably from about 30 percent to about 90 percent, and most preferably from 50 percent to 80 percent. The heavy hydrocarbon fraction preferably contains a concentration of olefinic compounds in an amount such that the weight of olefinic compounds as a percentage of the total weight of the heavy hydrocarbon fraction less than about 20 percent, more preferably less than about 5 percent, and most preferably less than 2 percent. The heavy hydrocarbon fraction preferably contains a concentration of sulfur of from about 10 ppmw to about 10,000 ppmw, more preferably from 100 ppmw to 2,000 ppmw.

Typically, the bulk of the organic sulfur compounds and aromatic compounds which are present in the full range hydrocarbon feed are located in the heavy hydrocarbon fraction, while only a small percentage of the olefins present in the full range hydrocarbon feed are located in the heavy hydrocarbon fraction. Preferably, the concentration (ppmw) of organic sulfur compounds in the heavy hydrocarbon fraction is more than about 150 percent of the concentration (ppmw) of organic sulfur

compounds in the full range hydrocarbon feed, more preferably more than about 300 percent, and most preferably more than 400 percent. Preferably, the concentration (wt. %) of aromatic compounds in the heavy hydrocarbon fraction is more than about 150 percent of the concentration (wt. %) of aromatic compounds in the full range hydrocarbon feed, more preferably more than about 200 percent, and most preferably more than 300 percent. Preferably, the concentration (wt. %) of olefinic compounds in the heavy hydrocarbon is less than about 50 percent of the concentration (wt. %) of olefinic compounds in the full range hydrocarbon feed, more preferably less than about 20 percent, and most preferably less than 5 percent.

The hydrodesulfurization process of the present invention can take place in any suitable reactor by contacting the hydrocarbon feed with the catalyst composition described in the first embodiment of the present invention under hydrodesulfurization conditions sufficient to convert at least a portion, preferably a substantial portion, of the organic sulfur compounds in the hydrocarbon feed to inorganic sulfur compounds, such as hydrogen sulfide. Suitable reactors include, for example, a fixed bed reactor system, hepulated bed reactor system, fluidized bed reactor system, moving bed, slurry reactor system, and the like. In the case of fixed bed reactor system, the reaction zone may consist of one or more fixed bed reactors and may comprise a plurality of catalyst beds. It is preferred to use extrudates, pellets, pills, spheres or granules of the catalyst in a fixed bed reactor system, under conditions where substantial feed vaporization occurs.

Hydrodesulfurization reaction conditions can include a reaction temperature of from about 100°C to about 500°C, preferably from 150°C to 400°C. The reaction pressure is preferably from about atmospheric pressure to about 5000 psig, more preferably from 50 psig to 2000 psig. The weighted hourly space velocity (WHSV) of the hydrocarbon feed is preferably from about 0.1 hr⁻¹ to about 10 hr⁻¹, more preferably from 0.2 hr⁻¹ to 5 hr⁻¹.

A hydrogen-containing stream can be added to the hydrocarbon feed prior to and/or during the hydrodesulfurization reaction. The hydrogen stream can be pure hydrogen or can be in admixture with other components found in refinery hydrogen streams. It is preferred that the hydrogen-containing stream contain little, if any, hydrogen sulfide. The hydrogen stream purity should be at least about 50% by volume hydrogen, preferably at least about 65% by volume hydrogen, and most preferably at least 75% by volume hydrogen for best results. The hydrogen to hydrocarbon ratio employed in the inventive hydrodesulfurization process is preferably from about 0.1:1 to about 100:1, more preferably from 0.2:1 to 50:1.

The hydrodesulfurized hydrocarbon product produced by the process of the fourth embodiment of the present invention comprises inorganic sulfur compounds, typically hydrogen sulfide. The inorganic sulfur compounds can be removed by any process known in the art before or after, preferably before, recombining the hydrodesulfurized heavy hydrocarbon fraction and the light hydrocarbon fraction. Conventional processes for removing inorganic sulfur compounds from a hydrocarbon stream include, for example, gas sparging, caustic

scrubbing, amine treating, absorption, flashing, and conventional gas-liquid separation.

The hydrodesulfurized heavy hydrocarbon product produced by the inventive process preferably contains a concentration (ppmw) of organic sulfur compounds which is less than about 25 percent of the concentration (ppmw) of organic sulfur compounds in the heavy hydrocarbon fraction fed to the reactor, more preferably less than about 15 percent, and most preferably less than 10 percent. The hydrodesulfurized heavy hydrocarbon product preferably contains a concentration (wt. %) of aromatic compounds that is more than about 90 percent of the concentration (wt. %) of aromatic compounds in the heavy hydrocarbon feed, more preferably more than about 95 percent, and most preferably more than 97 percent.

After the heavy hydrocarbon fraction has been hydrodesulfurized to produce a hydrodesulfurized heavy hydrocarbon product, the hydrodesulfurized heavy hydrocarbon product can be recombined with the light hydrocarbon fraction to produce a hydrodesulfurized full range hydrocarbon product. The hydrodesulfurized full range hydrocarbon product preferably has a concentration (ppmw) of organic sulfur compounds that is less than about 25 percent of the concentration (ppmw) of organic sulfur compounds in the full range hydrocarbon feed, more preferably less than about 10 percent, and most preferably less than 5 percent. The hydrodesulfurized full range hydrocarbon product preferably contains a concentration (wt. %) of aromatic compounds which is more than about 95 percent of the concentration (wt. %) of aromatic compounds in the full range hydrocarbon feed, preferably more than about

97 percent, most preferably more than 99 percent. The hydrodesulfurized full range hydrocarbon product preferably has a research octane number (RON) which is more than about 95 percent of the RON of the full range hydrocarbon feed, preferably more than about 97 percent, most preferably more than 99 percent.

5 The following examples are presented to further illustrate the invention and are not considered as limiting the scope of the invention.

Example I

This example demonstrates methods of preparing conventional and inventive hydrodesulfurization catalysts.

10 Catalyst A (conventional) was prepared by calcining and pre-sulfiding a commercially available CoMo/Al₂O₃ hydrodesulfurization catalyst ("TK-554", provided by Haldor-Topsoe, Inc., Houston, Texas). The commercial catalyst was calcined in air at 500° C for 3 hours. The calcined catalyst was then pre-sulfiding for 2 hours at 400° C with a carbon disulfide-saturated stream of hydrogen, flowing at 15 100 mL/min.

The resulting catalyst was designated Catalyst A.

20 Catalyst B was prepared by impregnating 23.27 grams of γ-alumina as 1/16 inch extrudate from Criterion Catalyst Company L.P. (Michigan City, Ind.) with 13.19 grams of an aqueous solution containing 25 wt.% cobalt nitrate, 15 wt.% ammonium heptamolybdate, and 20 wt.% citric acid. The impregnated extrudate was then calcined in air at 500°C for 3 hours. A 23.67 gram quantity of the calcined, impregnated extrudate was impregnated with 15.24 grams of an aqueous solution

containing 25 wt.% cobalt nitrate, 15 wt.% ammonium heptamolybdate, and 20 wt.% citric acid. The twice-impregnated extrudate was then calcined in air at 500° C for 3 hours. The resulting Co/Mo-modified catalyst contained 9.448 wt.% molybdenum and 5.818 wt.% cobalt. A 8.80 gram quantity of the Co/Mo-modified catalyst was pre-sulfided for 2 hours at 400° C with a carbon disulfide-saturated stream of hydrogen, flowing at 100 mL/min.

The resulting catalyst was designated Catalyst B.

Catalyst C was prepared by impregnating 23.27 grams of γ -alumina as 1/16 inch extrudate from Criterion Catalyst Company L.P. (Michigan City, Ind.) with 13.19 grams of an aqueous solution containing 25 wt.% cobalt nitrate, 15 wt.% ammonium heptamolybdate, and 20 wt.% citric acid. The impregnated catalyst was then calcined in air at 500° C for 3 hours. A 23.67 gram quantity of the calcined, impregnated extrudate was impregnated with 15.24 grams of an aqueous solution containing 25 wt.% cobalt nitrate, 15 wt.% ammonium heptamolybdate, and 20 wt.% citric acid. The twice-impregnated extrudate was then calcined in air at 500° C for 3 hours. The resulting Co/Mo-modified catalyst contained 9.448 wt.% molybdenum and 5.818 wt.% cobalt. A 17.60 gram quantity of the Co/Mo-modified catalyst was pre-nitrided for 2 hours at 700° C with ammonia flowing at 200 mL/min.

The resulting catalyst was designated Catalyst C.

Catalyst D was prepared by impregnating 23.27 grams of γ -alumina as 1/16 inch extrudate from Criterion Catalyst Company L.P. (Michigan City, Ind.) with 13.19 grams of an aqueous solution containing 25 wt.% cobalt nitrate, 15 wt.%

ammonium heptamolybdate, and 20 wt.% citric acid. The impregnated extrudate was then calcined in air at 500 °C for 3 hours. A 23.67 gram quantity of the calcined, impregnated extrudate was impregnated with 15.24 grams of an aqueous solution containing 25 wt.% cobalt nitrate, 15 wt.% ammonium heptamolybdate, and 20 wt.% citric acid. The twice-impregnated extrudate was then calcined in air at 500°C for 3 hours. The resulting Co/Mo-modified catalyst contained 9.448 wt.% molybdenum and 5.818 wt.% cobalt. A 17.60 gram quantity of the Co/Mo-modified catalyst was pre-nitrided for 2 hours at 700°C with ammonia flowing at 200 mL/hr. A 12.85 gram quantity of the nitrided Co/Mo catalyst was pre-sulfided for 2 hours at 400°C with a carbon disulfide-saturated stream of hydrogen, flowing at 100 mL/min.

The resulting catalyst was designated Catalyst D.

Example II

This example demonstrates that a pre-nitrided and pre-sulfided Co/Mo catalyst was highly effective for removing sulfur from the heavy fraction of catalytically cracked gas while retaining aromaticity.

Catalyst A (3.85 grams) was placed in a stainless steel reactor (1 inch inside diameter) between a top and bottom layer of "Alundum-36"™ (available from PQ Corporation, Valley Forge, Pennsylvania). The reactor was brought to hydrodesulfurization reaction conditions of 317° C and 500 psig. A heavy hydrocarbon feed was charged to the reactor at a weighted hourly space velocity (WHSV) of 1.039 h⁻¹. Hydrogen was co-fed to the reactor at a rate of 2.4 liters/hour. The heavy hydrocarbon feed was a heavy-cut of catalytically cracked gasoline which

had an initial boiling point of 244°F and a final boiling point of 489°F. The heavy hydrocarbon feed contained about 210 ppmw organic sulfur compounds, about 57 wt.% aromatics, about 1.5 wt.% olefins, about 8.0 wt.% naphthenes, about 14.0 wt.% iso-paraffins, about 3.7 wt.% paraffins, about 2.4 wt.% C₁₃⁺ hydrocarbons, and about 13.1 wt.% unknowns. Table I shows the hydrodesulfurization and hydrodearomatization characteristics of Catalyst A after 6.73 hours on stream.

Catalyst B (4.19 grams) was placed in the above-described reactor. The reactor was brought to hydrodesulfurization reaction conditions of 321° C and 451 psig. The same heavy hydrocarbon feed employed for Catalyst A was charged to the reactor at a WHSV of 0.955 h⁻¹. Hydrogen was co-fed to the reactor at a rate of 2.4 liters/hour. Table I shows the hydrodesulfurization and hydrodearomatization characteristics of Catalyst B after 6.00 hours on stream.

Catalyst C (4.04 grams) was placed in the above-described reactor. The reactor was brought to hydrodesulfurization reaction conditions of 322°C and 506 psig. The same heavy hydrocarbon feed employed for Catalyst A was charged to the reactor at a WHSV of 0.990 h⁻¹. Hydrogen was co-fed to the reactor at a rate of 2.4 liters/hour. Table I shows the hydrodesulfurization and hydrodearomatization characteristics of Catalyst C after 6.60 hours on stream.

Catalyst D (4.30 grams) was placed in the above-described reactor. The reactor was brought to hydrodesulfurization conditions of 319°C and 509 psig. The same heavy hydrocarbon feed employed for Catalyst A was charged to the reactor at a WHSV of 0.930 h⁻¹. Hydrogen was co-fed to the reactor at 2.4 liters/hour. Table

I shows the hydrodesulfurization and hydrodearomatization characteristics of Catalyst D after 6.55 hours on-stream.

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0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5 10.0
Time (hours)

Table I						
Catalyst	Support	Co/Mo Impregnations	Pre-Nitrided	Pre-Sulfided	Sulfur Removed (wt. %)	Aromatics Retained (wt. %)
A	γ -Al ₂ O ₃	--	—	—	90.0	91.2
B	γ -Al ₂ O ₃	2-Simultaneous	No	Yes	-5.2	92.7
C	γ -Al ₂ O ₃	2-Simultaneous	Yes	No	94.1	85.5
D	γ -Al ₂ O ₃	2-Simultaneous	Yes	Yes	90.7	97.7

The results in Table I demonstrate that a pre-nitrided Co/Mo catalyst was highly effective for removing sulfur from the heavy fraction of catalytically cracked gas while retaining aromaticity.